

Chloride **(BY DIGITAL CHLORIDOMETER)**

1. Application

This automated method is applicable to soil, tissue, waters (drinking, surface and saline waters), and domestic and industrial wastes.

2. Summary of Methods

Chloride is determined by an automatic chloride titrator (Digital chloridometer) by coulometric-amperometric titration with silver ions. In the chloride titrator, a constant direct current is passed between a pair of silver electrodes, causing release of silver ions into the titration solution at a constant rate. The silver ions react with chloride to precipitate ($\text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl}$). The end-point is after the increasing concentration of free silver ions cause a rising current to flow through a pair of silver indicator electrodes connected to a Meter-Relay. At a preset increment of indicator current the relay is actuated, stopping a timer, which runs concurrently with generation of silver ion. The amount of chloride precipitated is proportional to the elapsed time.

3. Safety

All chemicals should be considered a potential health hazard. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets should be made available to all personnel involved in the chemical analysis.

4. Interferences

- 4.1 Chloride from skin may contaminate samples, rubber gloves are necessary during handling of samples.
- 4.2 Acid washed filters must be used when filtering samples for chlorides. Unwashed filters contain varying amounts of chloride and will affect results.
- 4.3 Iodine, bromide, ferricyanide and ferric iron cause high results and must be removed. Chromate and dichromate should be reduced to chromic state or removed where contamination is minor. Some contaminants can be destroyed by adding nitric acid.

5. Sample Collection, Preservation and Handling

Soil and tissue samples are oven-dried at 55°C and ground to pass a 2-mm screen and stored in paper boxes (soil sample) or plastic bottles (for plant tissues). Water samples are stored at 4°C until analysis. Water samples should be completed within 28 days of the date of sampling.

6. Apparatus and Materials

- 6.1 Digital Chloridometer (LabConCo model # 442-5000)
- 6.2 Erlenmeyer flasks (125 ml)
- 6.3 Funnel tubes (15 ml)
- 6.4 Acid washed filter paper (9 cm Whatman No. 2 or equivalent). ★
- 6.5 Time-controlled oscillating shaker (Eberbach) set at 160 excursions per minute.
- 6.6 Glass vials (5 ml)
- 6.7 Disposable examination gloves
- 6.8 Balance – capable of 0.01 g



Hint: 6.4 For acid washed filters—use 10% Acetic Acid followed by 2 one-Liter DI rinses. Dry filters in oven.

7. Reagents

- 7.1 De-ionized water
- 7.2 Concentrated standard solution 0.1 N HNO₃ 10% CH₃COOH solution
- 7.3 1:1 glacial acetic acid / deionized water
- 7.4 Nitric-acid reagent (for tissue only) (0.1 N HNO₃ and 10% glacial acetic acid): To 900 ml of water, add 6.4 ml of concentrated nitric acid and 100 ml of glacial acetic acid. Volumes are approximate. (Acids should be reagent grade). Mix thoroughly.
- 7.5 Gelatin reagent (to 100ml of hot deionized water add 0.62 g of gelatin mixture (LabConCo gelatin reagent #442-5064), mix until dissolved. Reagent is good for six months if kept refrigerated)
- 7.6 Standard Chloride solution (0.0141 N NaCl). Dissolve 0.8241 g pre-dried (140°C) NaCl in deionized water, dilute to 1 liter (1 ml = 0.5 mg Cl⁻)
- 7.7 Reference solution (Environmental Resource Associates) Lot No. 99101



Hint: 7.5 Be sure gelatin reagent is at room temperature before using.

8. Methods

- 8.1 Weigh out 0.25-0.50 g (plant tissue), 0.4-0.5 g (for sandy soil) or 0.2-0.3 g (for silt, clay or muck soil) into a 125 Erlenmeyer flask. (For analysis of water, skip to step 8.4)
- 8.2 Add 10 ml of deionized water, plus 1 drop of 1:1 glacial acetic acid mixture to facilitate filtering.
- 8.3 Shake the suspension on an oscillating shaker, at 160 excursions per minute for 20 minutes, then filter. (Water samples high in suspended solids need filtering prior to analysis).
- 8.4 Transfer 3 ml of samples to glass vials, add 1 ml of (7.2) concentrated standard solution and 4 drops of (7.5) gelatin reagent.
- 8.5 Place glass vial on chloridometer, press start, when timer stops, record meg/L reading.



Hint: 8.1 Depending on the type of material: (ie manure sample wt=0.1g-0.2g)—run duplicate sample at different weight.

9. Calculations

Typical conditions for measuring low concentration of chloride over more than a hundredfold range are as follows:

ANTICIPATED CONCENTRATIONS* mEq/L

Conditions	Blank	0.05-0.9	0.9-5	5-30**
mL sample	0	3.0	0.5	0.1
mL .4 N HNO ₃				
40% CH ₃ COOH	1.0	1.0	1.0	1.0
Drops gelatin	4	4	4	4
mL distilled H ₂ O	3	0	2.5	3.0
Total volume	4.0	4.0	4.0	4.1
Display reading	-	15-270	45-250	50-300
Correction factor	--	1/300	1/50	1/10

* Assumes using **LOW** range in all cases.

** Concentrations in this range can use the serial titration procedure and the standard acid solution.

CORRECTION FORMULA FOR CONVERTING DISPLAY UNITS

For solid samples: mEqCl/L to %NaCl:

$$\% \text{NaCl} = \frac{(\text{reading})(5.85)(\text{final sample volumes, liters})}{\text{original sample weight, grams}}$$

This assumes a known weight of a solid sample has been mixed in a known final volume of solution.

For liquid samples:

$$\% \text{NaCl} = \frac{(\text{reading})(5.85)(\text{final sample volumes, liters})}{(\text{sample volume, liters})(\text{density g/L})}$$

mEq Cl/L to mg NaCl/L: mg NaCl/L = (reading x 58.5)

mEq Cl/L to ppm Cl: ppm Cl = (reading) x 35.5

10. Quality Control

10.1 Standard reference material from Lab Chem Inc. (LC13010-1) is analyzed with each run as well as reagent blanks.

11. Reporting

11.1 Samples are reported in ppm Cl⁻ ± 0.5

12. Reference

Adapted from Standard methods for the Examination of Water and Wastewater, 15th Edition, 1980, (pgs 273-275). Method 407C